SCIENCE FOR CERAMIC PRODUCTION

SYNTHESIS OF ZIRCONIUM DIOXIDE MICROFIBER FROM AQUEOUS SOLUTIONS

V. V. Guzeev[1] and A. N. D'yachenko[1]

A technology for producing filamentary crystals of zirconium dioxide for the production of high-strength ceramics is developed. Comparative characteristics of the methods of precipitation of zirconium oxychloride crystals by chilling a supersaturated solution and salting out using hydrochloric acid are provided. A method for producing filamentary crystals of zirconium dioxide from oxychloride without using high temperatures and pressure is analyzed.

The production of crystalline materials in the form of filamentary crystals is of great interest. Filamentary crystals (microfibers) have found application in the production of construction ceramics and reinforcement of metal alloys. In spite of the great demand for filamentary crystals, there is yet no industrial technology for the production of microfibers.

Filamentary crystals of chemical compounds and metals are currently produced using gas-phase reactions at high temperatures: 700 – 1200°C.

Analyzing the physical properties of different compounds [1, 2], it can be observed that a filamentary shape is inherent in highly hydrated molecules and polyatomic compounds, as well as in certain halides of *d*-metals. This makes it possible to assume that filamentary crystalline structures arise due to a weak and loose energy bond, which imparts an elongated dipole shape to these structure. Indeed, ligands or outer hydrate layers in large complex molecules and in hydrates can easily separate from the main molecule and even have a variable composition. These properties prevent using them in engineering. Some halides of *d*-metals combine the useful properties of a loose energy bond leading to the formation of a filamentary structure and a compact size of the molecule that does not disintegrate under thermal action. It is precisely compounds of *d*-metals, in particular microfibers of zirconium and titanium dioxides, that are of special interest for industrial technologies.

The similarity of these compounds to large complexes and hydrates can be explained as follows:. Halogens have larger radii of atoms and ions than other elements. It is known that the chemical activity of any compound depends on the energy of its outer shell; the outer shell of an atom is an electron, that of a complex is a ligand, and that of a hydrate is a molecule of water. Consequently, halogens in their chemical activity are comparable with complexes and hydrates, and the larger the radius of a halogen atom (ion), the more distinct is the stretching of the molecule and the more perfect is its crystal structure. Considering the sequence of *d*-metal halides, it can be easily observed that nearly all iodides are synthesized in the form of filamentary crystals, the majority of bromides are also crystallized in the shape of needles, chlorides have a greater variety of crystal structures, and some of them are liquid. The higher fluorides at normal and especially at elevated temperatures occasionally exist as gaseous compounds.

The described properties corroborate the assumption that filamentary crystallization occurs in the case of weak external energy level of coupling. Indeed, the radius of the halogen atoms increases from fluorine to iodine and, accordingly, the surface charge decreases. With a relatively small surface charge, each molecule cannot be independent, and a mixture of interrelated anions and cations is formed, which produce a crystal. With the radius of the halogen is small, as in fluorine, the value of the surface charge is sufficient to strongly retain its cation. Such molecules are neutral, do not need joining with other molecules, and form rather inert gaseous formations. When a crystal seed is formed, an enhanced charge density arises on one of the sharper ribs of this seed and the subsequent molecules become attracted to that spot, which further increases the charge density, and the crystal keeps growing in that direction.

[1] Tomsk Polytechnic University, Tomsk, Russia.
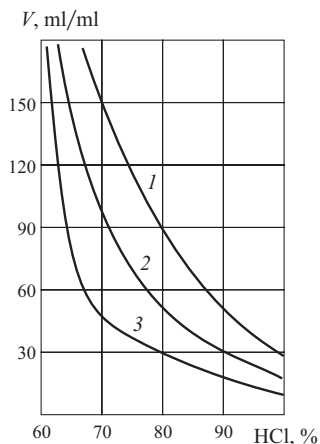
Fig. 1. The amount of acid introduced depending on its concentration: *1*, *2*, and *3*) 900, 1300, and 1700 g/liter of zirconium oxychloride, respectively.

The cheapest and most widely available halides are chlorides; they are industrially produced and can be the most expedient basis for the development of the technology of producing filamentary crystals. In the slow crystallization of a supersaturated solution of zirconium oxychloride, the latter settles in the shape of thin long needles which can be easily separated from the matrix solution by filtration. Crystallization of zirconium oxychloride can be carried out by two methods: crystallization in chilling or salting-out crystallization using hydrochloric acid.

The crystallization method used in industrial practice involves chilling of a heated supersaturated solution to room temperature; however, this method does not allow one to control the length of the crystals. The resulting microfibers of zirconium oxychloride octahydrate are up to 3 mm long and $100 - 500$ μm in diameter. Such dimensions are too large; after elongation a crystal starts growing thick and changes its characteristics, which could be due to a slow decrease in the temperature and, accordingly, the formation of a relatively small number of crystallization centers, which determine the quantity and the size of crystals.

Crystallization by salting out based on hydrochloric acid is used as well. The solubility of zirconium oxychloride in pure water at 20°C is 939 g/liter; then, with increasing concentration of hydrochloric acid, the solubility drops abruptly, and salting out, i.e., precipitation of $ZrOCl_2 \cdot 8H_2O$ crystals, takes place. Complete crystallization proceeds in several microseconds, virtually instantly. Accordingly, the rate of crystal growth reaches several millimeters per second. At such growth rates a crystal keeps growing along the active centers, which means only in length. Within such short time interval, defects leading to thickening of crystals do not have time to emerge. An enormous quantity of crystallization centers is instantly formed in the total volume of the solution, which ensures the formation of microfibers of length under 100 μm long and about 1 μm in diameter. When a concentrated hydrochloric acid is used, lumps of difficulty filterable crystals

are formed in the contact site of the acid with the solution. To prevent this, the acid is diluted and added to the solution, which is intensely stirred.

Three intensely stirred aqueous solutions of zirconium oxychloride with a concentration of 900, 1300, and 1700 g/liter were prepared, for which purpose hydrochloric acid of known concentration was added from a burette in drops to an aqueous solution. When the amount of acid is insufficient, no crystals are salted out, and after a certain quantity of acid is introduced, instantaneous crystallization of the solution is observed.

The dependence of the amount of added acid on the concentration necessary to ensure crystallization in plotted in Fig. 1.

Use of hydrochloric acid at a concentration below 60% does not cause salting out and crystallization of zirconium oxychloride at all. Based on the results of the experiments performed, it is possible to recommend an optimum salting-out regime. It is convenient to use supersaturated aqueous solutions of concentration of $1000 - 1500$ g/liter for salting out zirconium oxychloride at a temperature of $20 - 25$°C. To reduce the corrosion of the equipment, it is recommended to use 70% hydrochloric acid. The amount of acid to be added can be calculated based on the data in Fig. 1.

Rapid introduction and intense mixing of a calculated amount of hydrochloric acid and zirconium oxychloride solution for $30 - 60$ sec produces salting out of $ZrOCl_2 \cdot 8H_2O$ crystals and solidifying of the solution.

The obtained microfibers of zirconium oxychloride octahydrate have to be transformed into zirconium dioxide with conservation of their monocrystalline structure. Under certain conditions oxychloride crystals after heating and dehydration preserved the needle shape, which also did not change after calcination of oxychloride to dioxide.

Experimental studies indicated that the particle size has a significant effect on the quality of the resulting zirconium dioxide. The smaller the fiber diameter, the better the crystal structure of the product is preserved after calcination. This can be accounted for by the process mechanism. The dehydration of zirconium oxychloride octahydrate involved two processes: evaporation of moisture and dissolution of the upper layers of oxychloride in water vapor released from the bottom layers.

In order to prevent the second (undesirable) process, it is necessary to ensure the minimum possible size of the crystals and the minimum possible thickness of the poured layer. The thickness of the bulk layer in the experiments was equal to several crystals, which made it possible to avoid the dissolution of the upper crystals in the vapor released. If the diameter of the crystal is less than 5 μm, its crystal structure is fully preserved. When the particle diameter is over 50 μm, the crystal is destroyed and fused.
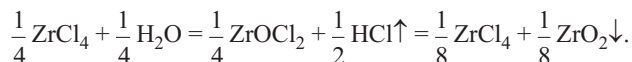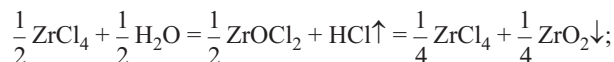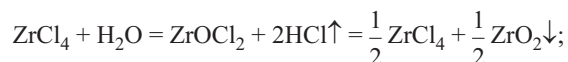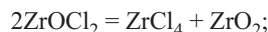
Since the first calcination temperature does not exceed 250°C, the process of slow calcination in a thin layer can be implemented in a conveyor furnace or in a suspended layer.

The next stage after dehydration is the transformation of anhydrous zirconium oxychloride into zirconium dioxide. When heated in air, zirconium oxychloride decomposes into zirconium tetrachloride and zirconium dioxide [2]:

$$2ZrOCl_2 \rightarrow ZrCl_4 + ZrO_2.$$

In slow heating, zirconium tetrachloride and dioxide are formed. Tetrachloride is hydrolyzed with the remaining crystallization water and is again transformed into oxychloride. In principle this process is cyclic and can be repeated in each heating and cooling.

The true mechanism of the destruction of a molecule of zirconium hydrochloride octahydrate is presumably of a complex stepwise nature. The following scheme of decomposition of oxychloride can be suggested. First, the compound decomposes into an oxide and a tetrachloride, then the tetrachloride reacts with moisture released in dehydration and again transforms into an oxychloride. A chain reaction is started, which leads to complete conversion of oxychloride into oxide and release of hydrogen chloride.

$$2ZrOCl_2 = ZrCl_4 + ZrO_2;$$

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl\uparrow = \frac{1}{2}ZrCl_4 + \frac{1}{2}ZrO_2\downarrow;$$

$$\frac{1}{2}ZrCl_4 + \frac{1}{2}H_2O = \frac{1}{2}ZrOCl_2 + HCl\uparrow = \frac{1}{4}ZrCl_4 + \frac{1}{4}ZrO_2\downarrow;$$

$$\frac{1}{4}ZrCl_4 + \frac{1}{4}H_2O = \frac{1}{4}ZrOCl_2 + \frac{1}{2}HCl\uparrow = \frac{1}{8}ZrCl_4 + \frac{1}{8}ZrO_2\downarrow.$$

The summary reaction in this case will be as follows:

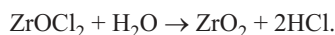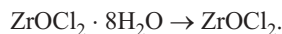$$ZrOCl_2 + H_2O \rightarrow ZrO_2 + 2HCl.$$

Figure 2 shows the derivatogram of the process of thermal decomposition of zirconium oxychloride octahydrate. Three endothermic and one exothermic effects are registered in the DTA curve. The first endothermic effect has a peak at 70°C and correlates with the loss of hygroscopic moisture. The second and third endothermic effects are caused by the two-stage loss of crystallization water

$$ZrOCl_2 \cdot 8H_2O \rightarrow ZrOCl_2.$$

The exothermic effects correlates with the reaction of replacement of chlorine with oxygen and the formation of zirconium dioxide at 455°C.

The rate of variation in the weight of calcined materials depending on the process temperature was investigated. In each experiment a sample (100 mg of $ZrOCl_2 \cdot 8H_2O$) was placed into a furnace with a constant temperature of 200, 300, 400, and 500°C and the time dependence of the weight variation was registered (Fig. 3).
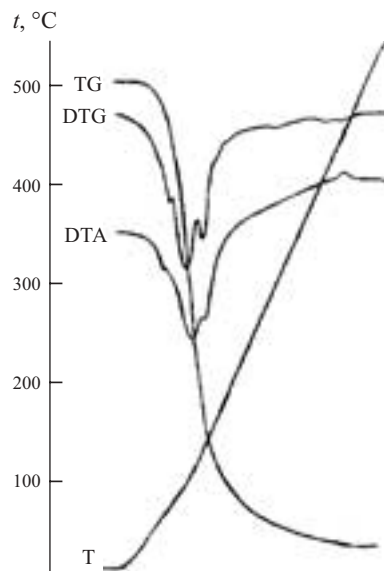

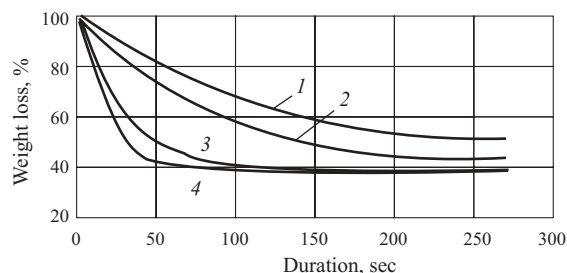**Fig. 2.** The derivatogram of the process of thermal decomposition of zirconium oxychloride octahydrate.

Fig. 3. Kinetic curves of calcination of octahydrate of zirconium oxychloride: *1*, *2*, *3*, and *4*) temperatures of 200, 300, 400, and 500°C, respectively.

It can be seen that at 200°C the weight of the material decreases to 55% of the initial level, which correlates with the transformation of $ZrOCl_2 \cdot 8H_2O \rightarrow ZrOCl_2$; at 500°C the weight of the material drops to 38% of the initial value, which correlates with the transition $ZrOCl_2 \cdot 8H_2O \rightarrow ZrO_2$. It is established that in calcination within the temperature interval of 200 – 500°C, the weight of the sample was stabilized and amounted to 38 – 55% depending on the calcination temperature, which correlated with the course of heating of a certain equilibrium mixture $ZrOCl_2 \cdot ZrO_2$ and a gradual accumulation of ZrO_2 in $ZrOCl_2$ with increasing temperature.

The kinetic curves were used to calculate the apparent activation energy for the first process, i.e., dehydration. It was equal to 4.2 kJ/mole, which indicates the external diffusion mechanism of the process (the curves were processed using the Yander equation [3]). When zirconium oxychloride octahydrate is heated to 200°C, the desorption of crystallization water takes place. At a temperature over 300°C, the ex-

ternal diffusion mechanism with an apparent activation energy of 12.8 kJ/mole prevails.

The identification of the reaction mechanisms and the apparent activation energy for the considered process is arbitrary, as the final product has a different composition at each temperature.

The most significant result of the kinetic studies is the determination of the high rate of the reaction: at a high temperature (400°C) the reaction ended in 50 sec, and at a low temperature (100°C) it took 200 sec. The reaction duration largely depends on the thickness of the poured layer of the powder and the gas flow rate above that layer.

After two-stage calcination, zirconium dioxide microfibers of virtually monocrystalline structure were obtained.

REFERENCES

1. G. Brauer, *A Manual in Inorganic Synthesis, Vol. 5* [Russian translation], Mir, Moscow (1985).
2. *Chemistry and Technology of Rare and Scattered Elements, Vol. 2* [in Russian], Vysshaya Shkola, Moscow (1976).
3. F. Habashi, *Principles of Applied Metallurgy, Vol. 1* [Russian translation], Metallurgiya, Moscow (1975).